

The gas-phase photoemission beamline at Elettra

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(Received 4 August 1997; accepted 9 January 1998)

This paper reports the present stage of commissioning of the gas-phase photoemission beamline at Elettra, Trieste. The beamline is designed for atomic and molecular science experiments with high-resolution and high-flux synchrotron radiation. It consists of an undulator source, variable-angle spherical-grating monochromator and two experimental stations. The design value of the energy range is 20 to 800 eV with a specified resolving power of over 10000. The procedure adopted for calibration of this type of monochromator is discussed. At present a resolving power up to 20000 and a range up to 900 eV have been measured. Absorption spectra taken at the argon $L_{II,III}$ -edge and at the nitrogen, oxygen and neon K -edges are as sharp as, or sharper than, any reported in the literature. The instrumental broadening is well below the natural line-width making it difficult to quantify the resolution; this problem is discussed.

Keywords: gas-phase photoemission; energy resolution.

1. Introduction

In this paper we give a brief summary of the procedures which have been used and the results obtained during the commissioning of the gas-phase photoemission beamline at Elettra. This beamline is designed to operate with two experimental stations that can be connected alternately, and are devoted to angle-resolved photoemission spectroscopy and electron–electron coincidence spectroscopy. We concentrate on the monochromator as this is in the most advanced stage of commissioning. The optical concept has been described previously (Melpignano *et al.*, 1995) and consists of a variable-angle spherical-grating monochromator, with pre-focusing and post-focusing optics before and after the entrance and exit slits, respectively, as shown in Fig. 1. The complexity of having two movable optical elements between these

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slits, a plane mirror and a grating, means that the instrument is more difficult to calibrate. However, the design provides the considerable advantage of a fixed focus in the experimental chamber, which is particularly useful from the point of view of gas-phase and coincidence experiments. In the beamline described here, one of the experimental chambers has ten electron-energy analysers focused on the light spot. Details are given elsewhere (Prince *et al.*, 1997).

Both energy calibration and resolution measurement were carried out using gas-phase absorption spectra. They were taken using a two-plate windowless ionization chamber, with an aperture of 2 mm and active length of about 10 cm; the chamber was separated from the beamline by differential pumping. Typical dwell time was 1–3 s, and the monochromator entrance and exit slit settings were 10 μ m. A removable photodiode at the exit of the gas cell monitored the transmitted beam current to ensure that the spectrum was always in the linear absorption regime. This is important as excessive pressure in the gas cell causes it to function in the non-linear regime and gives an apparent reduction of the resolution.

2. Alignment and calibration procedure

The first step was to verify the parallelism of the axes of rotation of the optical elements, which was checked with an in-house procedure described elsewhere (Qian & Sostero, 1998).

The second problem was to attain the specified resolution, which was initially limited by mechanical accuracy due to backlash *etc.* The problem of maximizing resolution is intimately linked with the problem of how to calibrate the energy scale. There are an infinite number of pairs of grating and mirror angles which will give a specified photon energy, but only one of these pairs will minimize the defocus term and thus maximize the resolution. Due to the simultaneous movement of mirror and grating, mechanical imperfections such as backlash, imprecision and reading accuracy contribute twice to a reduction of the resolution. Noticeable improvement was obtained by moving only one optical element, the grating. It can be shown that the defocus term changes slowly near the optimum value, thereby justifying the use of a fixed mirror in a limited energy range. In such a mode, higher resolution can be achieved, although in a limited tuning range (for instance, about 6 eV range at 400 eV, which is sufficient to scan in detail a resonance profile). Our procedure was therefore to measure a known sharp absorption spectrum at a particular mirror setting, to determine the resolution and then repeat the procedure for a number of mirror settings. As a concrete example, the nitrogen absorption spectrum near 401 eV is shown in Fig. 2. A series of similar spectra were taken at different mirror settings and therefore with varying resolution. The third-peak to first-valley intensity ratio was then used as a resolution indicator and was plotted against the mirror setting, as shown in Fig. 3. The measured quantity consists of two components: (i) the defocus contribution to the instrumental resolution, which changes with mirror setting, and (ii) the natural line-width and other contributions to resolution, which are constant as the mirror setting is changed. The total width can be approximated by a sum in quadrature and has a roughly parabolic shape. The minimum of this curve gives the mirror setting at which the defocus term is minimized and thus the best resolution for the energy of that

Table 1
Measured line widths, including instrumental broadening.

Line	Width (meV)	Natural line-width (meV)	Reference
Ar $2p_{3/2}-4s$	116	116 ± 3	King & Read (1985)
		114 ± 2	Sairanen <i>et al.</i> (1996)
		130	Quaresima <i>et al.</i> (1995)
N $1s-\pi^*$, $n' = 0$ vibrational state	118	123 ± 10	Hitchcock & Brion (1980)
		128	Quaresima <i>et al.</i> (1995)
O $1s-\pi^*$, $n' = 3$ vibrational state	187	196	Hitchcock & Brion (1980)
Ne $1s-3p$, first order	275	230 ± 20	Hitchcock & Brion (1980), Ma <i>et al.</i> (1991), Gelius <i>et al.</i> (1974)
Ne $1s-3p$, second order	258	320	Domke <i>et al.</i> (1992)

absorption edge. The energy scale has been calibrated against the EELS values of the excitation energies given by King *et al.* (1977) for the first and fourth peaks.

3. Energy resolution results

Having performed the above procedure at each edge, the best resolution was obtained.

At energies below about 80 eV, lifetime widths of some noble gas absorption lines are small and it is not difficult to measure instrumental resolution. At 65 eV for instance, we have resolved the twentieth peak in the $N = 2$ series of the autoionization double-excitation states of He, which indicates a resolving power of 20000 at this energy (Domke *et al.*, 1991). In the near future we will be testing the resolving power down to 20 eV, the minimum specified energy.

There are a number of standard gas-phase absorption spectra which are typically used to assess the energy resolution of soft X-ray monochromators, and examples at higher energy are shown in Figs. 4–8. To our knowledge the best-resolved published spectrum of the argon $L_{II,III}$ -edge is that of Sairanen *et al.* (1996). They deduced a value of 114 ± 2 meV for the width of the $2p_{3/2}-4s$ resonance from a measured peak 118 meV wide (Aksela, 1997). Our spectrum, Fig. 4, has a slightly narrower measured width of 116 meV, but the numerical difference between the results may not be significant. A clearer indication of spectral quality is given by the fact that we resolve the $2p_{1/2}-7d$ peak, Fig. 5, which was not observed previously. This implies we have slightly better resolution, but it is difficult to quantify the difference.

The oxygen K -edge absorption spectrum, Fig. 6, shows partial resolution of the vibrational structure, which was not resolved by Ma *et al.* (1991) or Domke *et al.* (1992). The central part of the spectrum shown was fitted with six lines, and this is sufficient to extract the Lorentzian width. The whole spectrum can be fitted

with larger numbers of lines but then assumptions have to be made about the unresolved lines, *e.g.* that their spacing and width are constant. By fitting only the central part where the lines are partially resolved, a reliable value of the width can be extracted. The Rydberg states have also been measured (not shown) and closely resemble the spectra of Yagashita *et al.* (1994), who reported a resolving power of 10000. The Ne K -edge spectrum, Fig. 7, was taken in the first diffraction order (fifth harmonic of the undulator) and in the second-order (shown in Fig. 7, normalized to the flux). The $6p$ state, although weak, is reproducibly observed. The intensity above the threshold is artificially low due to the normalization being imperfect: the flux is changing rapidly in this region due to the nickel coating on the grating, and normalization is difficult.

Table 1 summarizes the experimentally measured widths of the selected lines, together with the corresponding natural line-widths taken from the literature. It is now clear that, at very high resolution, when the intrinsic width is comparable with the total absorption line-width, it is difficult to extract good values for the resolution. Indeed it is not reliable to fit the spectrum with a Voigt line shape and assume the Gaussian component represents the resolution. The problem is that at very high resolution the two widths are correlated and the peaks can be fitted with a pure Lorentzian to give an adequate (but not best) fit, but the fit improves slightly as the Gaussian is mixed in. On the other hand, above a certain value for the Gaussian the fit quality begins to deteriorate rapidly, as a narrow peak cannot be represented by a broad peak.

In Fig. 8 we show the results of a series of fits. The spectrum of nitrogen, Fig. 2, was fitted with a set of peaks with a Doniach–Sunjic line shape (Doniach & Sunjic, 1970); this somewhat unusual shape was chosen as we wished to check for asymmetries in the line shape, which can arise from optical aberrations or imperfect normalization. The spectrum was fitted to obtain convergence, leaving all parameters free except for

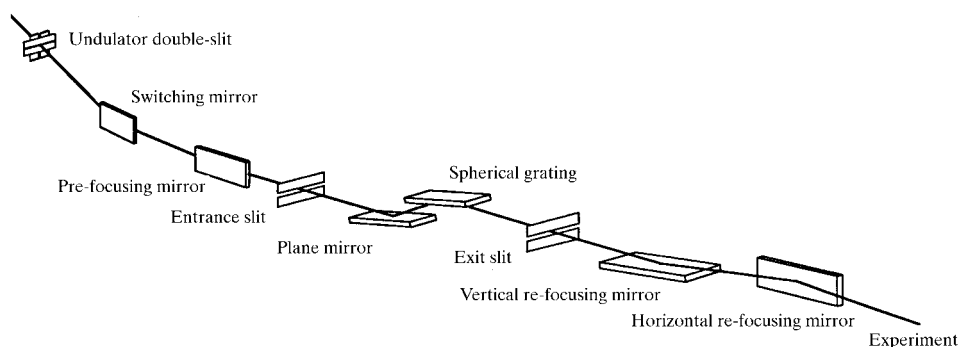
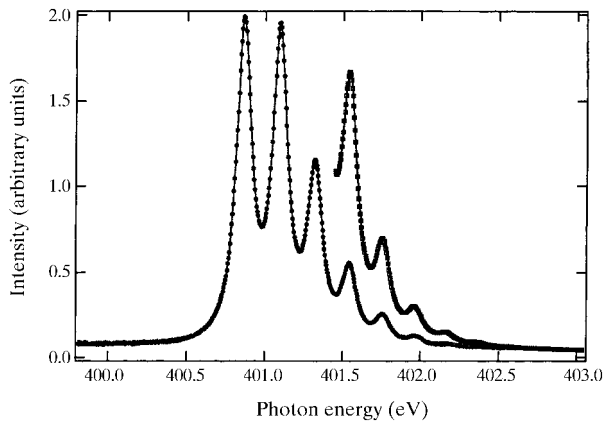
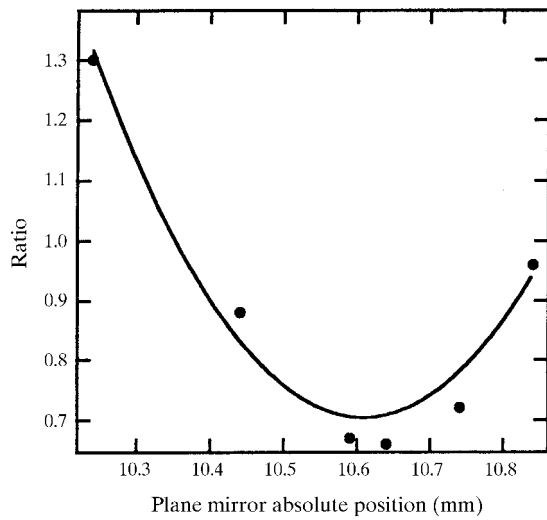


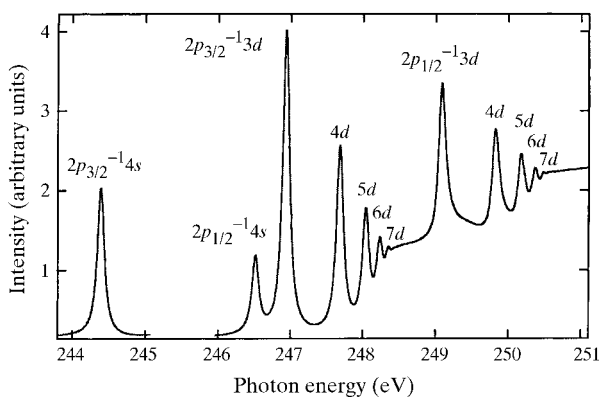
Figure 1
Schematic diagram of the optical layout of the gas-phase beamline.

**Figure 2**

Nitrogen absorption spectrum at the K -edge, $1s-\pi^*$ transition. The enlarged part of the spectrum was obtained with increased gas pressure and shows the higher vibrational states.

**Figure 3**

Resolution as a function of mirror setting. The index of resolution is the third-peak to first-valley ratio, and is plotted against the mirror position. Points: experimental data; line: fitted parabola.

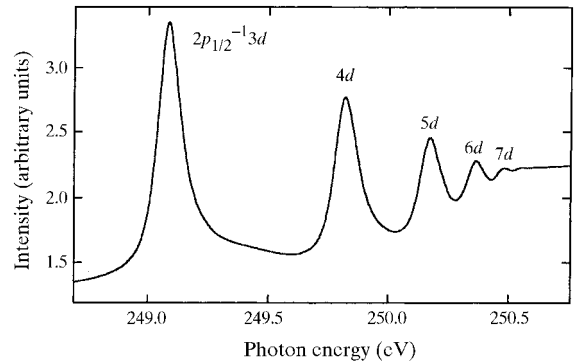
**Figure 4**

Absorption spectrum of argon at the $L_{II,III}$ -edge. The spectrum was taken in two parts, with a different undulator gap for each part, and normalized to the flux. The final-state assignments are shown.

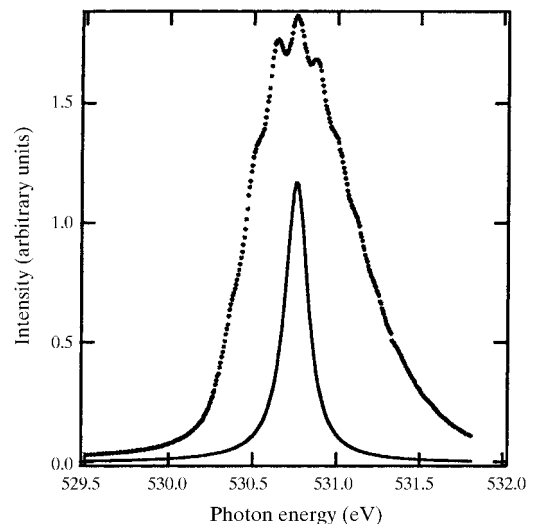
either the Gaussian or Lorentzian widths. These are highly correlated and the fit does not converge well if both are left free simultaneously. The asymmetry parameter was found to be 0.01 which means that the peaks are in fact practically a set of pure Voigt functions. Then the asymmetry was fixed and fits performed with fixed values of the Gaussian line-width so that the values of the Lorentzian width and χ^2 were extracted (Fig. 8). The minimum is rather broad and we tentatively give the resolution as 25 ± 5 meV, equal to a resolving power of $16000 (-3000/+4000)$, but any value under 40 meV gives an acceptable fit. Others have quoted similar resolving powers with less resolved spectra. Thus with the current generation of soft X-ray monochromators, it is becoming increasingly difficult to extract instrumental broadening from experimental spectra, which are dominated by intrinsic lifetime broadening.

4. Summary

The present work indicates that with the high resolution achievable with this modern monochromator, the experimental broadening makes only a minor contribution to the observed line-widths for core excitation processes in the soft X-ray range. This makes the measurement of the resolution by means of photoabsorption more difficult. In some cases, the present line-widths cast doubt on

**Figure 5**

Enlargement of the $2p_{1/2}-nd$ region, $n = 3-7$.

**Figure 6**

Oxygen K -edge spectrum, $1s-\pi^*$ transition. The central part of the spectrum was fitted with six individual peaks. Below the spectrum the fit curve of the $n = 4$ peak is shown; the other lines are omitted for clarity.

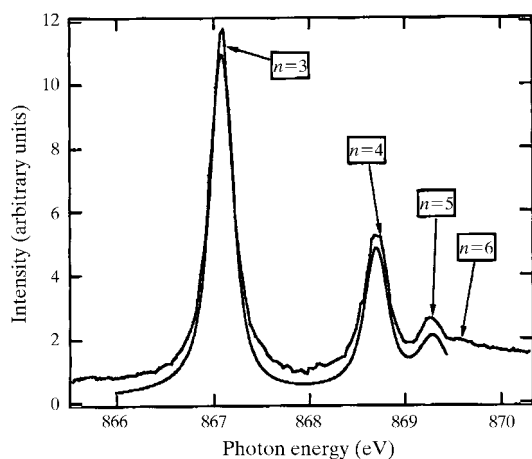


Figure 7

Spectrum at the Ne *K*-edge. Smooth line: fitted curve. The fitted curve has been displaced by 0.5 units on the vertical scale for clarity. The final-state assignments are shown for the excitations $1s\text{-}np$.

the values of the lifetime broadening reported in the literature, measured with electron energy-loss spectroscopy or photo-absorption. New experimental procedures and more accurate natural line-widths are needed in order to establish reliable values of the resolving power of this new class of instrument. In conclusion, excellent results have been obtained from the gas-phase photoemission beamline in terms of resolution. It is characterized by a resolving power well above the design value of 10000 over an extended range of soft X-ray energies.

We thank our colleagues at Elettra for their help and support, in particular F. Wei and A. Abrami and their groups, and F. De Bona and F. Mazzolini. In addition we thank J. Karvonen for experimental assistance. JS acknowledges support by the European Commission under contract number CIPA-CT94-0217.

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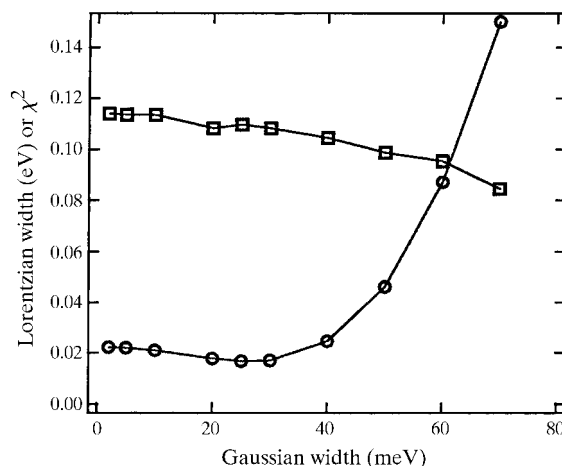


Figure 8

Values of the fitted Lorentzian width (squares) of the spectrum in Fig. 3 and χ^2 (circles) as a function of the fixed Gaussian width. In each fit the only other parameter held fixed was the asymmetry parameter.

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